Close-Proximity Electromagnetic Carbonization (CPEC)

(*Low Temperature Carbonization, LTC*)

Mat122

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Overview

Timeline

- Project Start: 10/1/15
- Project End: 9/30/20*
- Progress: 100%

*This project had two extensions:

- FY19 at no additional cost
- FY20 with additional costs

Budget

Initial budget planning

- FY16 – FY19: $4.5M

Effective budget:

- Funding received in FY16: $1.5M
- Funding for FY17: $1.35M (10% cut)
- Funding for FY18: $1.5M
- Funding for FY19: $0 (ext. at no add. costs)
- Funding for FY20: $1.0M

Barriers

- Barriers addressed
  - Cost: A goal of this project is to reduce energy consumption in the carbon fiber conversion process and therefore total carbon fiber cost.
  - Inadequate supply base: Another goal of this project is to reduce the required processing time for carbonization and therefore increase overall throughput.

2017 U.S. DRIVE MTT Roadmap Report, section 4

Partners

- Project lead: ORNL
- Partner: 4X Technologies

(formerly RMX Technologies)

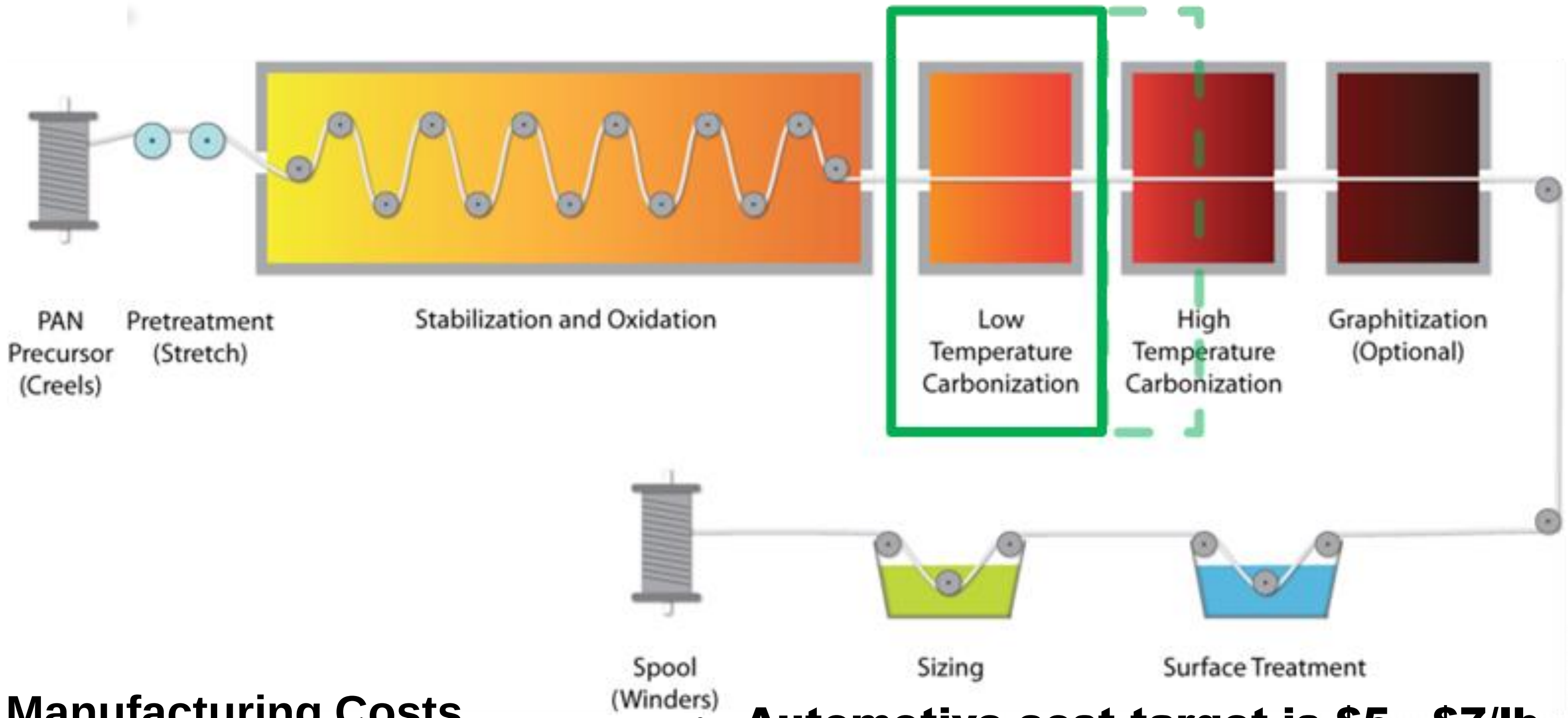
Relevance

- Project title:
  Close Proximity Electromagnetic Carbonization (CPEC):
  - Low temperature carbonization process (LTC)
  - Relies on dielectric heating (no convection)
  - Faster and more efficient that conventional
  - At atmospheric pressure
- Project Goals:
  - Reduce unit energy consumption of LTC stage (kWh/kg) by ca. 50% (ca. 5% of the cost reduction on the carbon fiber (CF) overall manufacturing process)
  - Produce equal or better quality carbon fiber
  - Scale the technology to a nameplate capacity up to one annual metric ton by project end date

Milestones

Date	Milestone	Status
March 31, 2019	**M13:** Hardware modification completed	**Completed: Apr. 27, 2020**
June 30, 2020	**M14:** 4 tows processed (final CF: strength = 250 ksi, Modulus = 25 Msi).	**Completed: June. 30, 2020**
Aug. 31, 2020	**M15:** 4 tows processed (final CF: strength = 250 ksi, Modulus = 25 Msi, residence time < 1min).	**Completed: Aug. 31, 2020**
Sept. 30, 2020	**M16:** Unit energy consumption of LTC by ca. 50% when compared to conventional LTC	**Completed: Sept. 30, 2020**

Approach (conventional PAN processing)



Major Manufacturing Costs

Precursor	ca. 43%
Oxidative stabilization	18%
Carbonization	13%
Graphitization	15%
Other	11%

- **Automotive cost target is $5 - $7/lb**
- **Tensile property requirements are 250 ksi, 25 Msi, 1% ultimate strain**
- **ORNL is developing major technological breakthroughs for major cost elements**

Approach (CPEC)

- Conventional furnaces consume significant energy heating large volumes of inert gas surrounding the fiber
- If thermal energy could be directly coupled from an energy source to the fiber, tremendous energy savings could be realized
- This project uses electromagnetic coupling to directly heat the fiber – not the surroundings (hardware, gas, etc.)
- Dielectric/Maxwell-Wagner heating mechanisms are utilized:

$$P_v = 2\pi f|E|^2\varepsilon_0\varepsilon' tan\delta$$

  - P_v volumetric power transferred to the material.
  - ε' is the relative dielectric constant.
  - ε_0 is permittivity of free space, 8.85418782 x 10^{-12} F/m.
  - $|E|$ is the magnitude of the local electric field intensity (V/m).
  - $tan\delta$ is the loss tangent of the material.
  - f is the operational frequency.

Historical development

- Project flow:

Material measurement → Computational Electromagnetic Modeling [CEM] (CPEC-2V) → Prototype design and build (CPEC-3) → Prototype tested → Prototype altered → Fiber production, Material characterization → CEM for CPEC-4 → Construction of CPEC-4 → CPEC-4 Commission and alteration → Traces of carbonization detected; Equipment failure → Upgrade: 2 new configurations → Selection of one configuration → Operation With multiple tows (up to 7) → SUCCESS

(Comsol vs. CST)

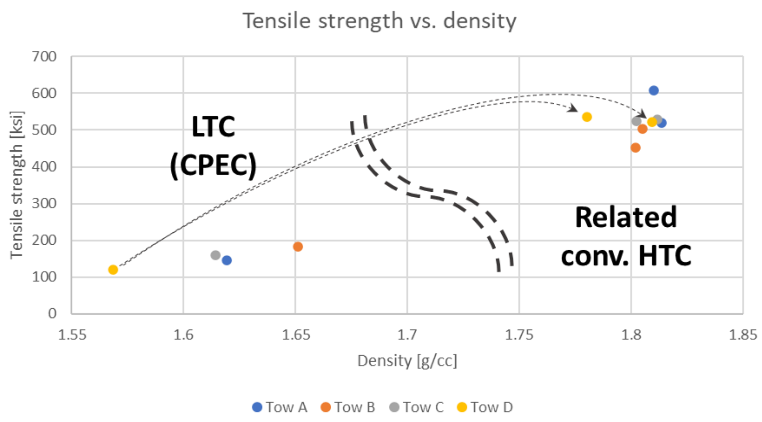
April – September 2020

Basic idea/confirmation (with CPEC-1, 2014-2015)

- Main achievements:
  - Material measurement/data acquisition (FY16)
  - CPEC-3 (FY17): demonstration of feasibility on batch or continuous process (one tow of 24k)
  - CPEC-4: Process with up to 7 continuous 50k tows

Progress — Operation of CPEC-4 Configuration #2

- Typical fiber properties of 4 tows (50k ea.) processed simultaneously

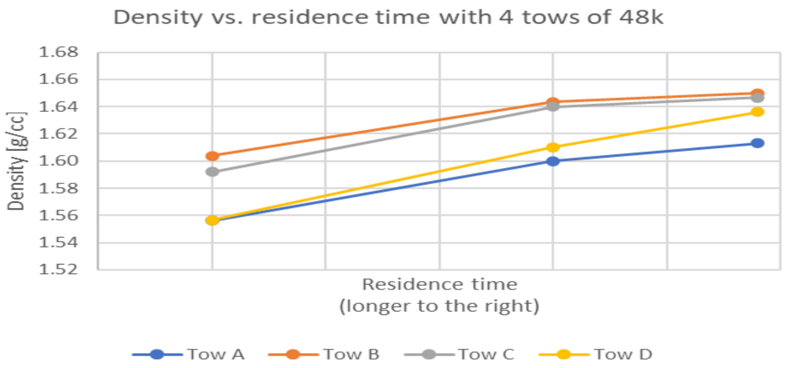


Tensile strength vs. density of carbonized material.

Fiber initially LTC carbonized via CPEC and subsequently HTC conventionally carbonized.

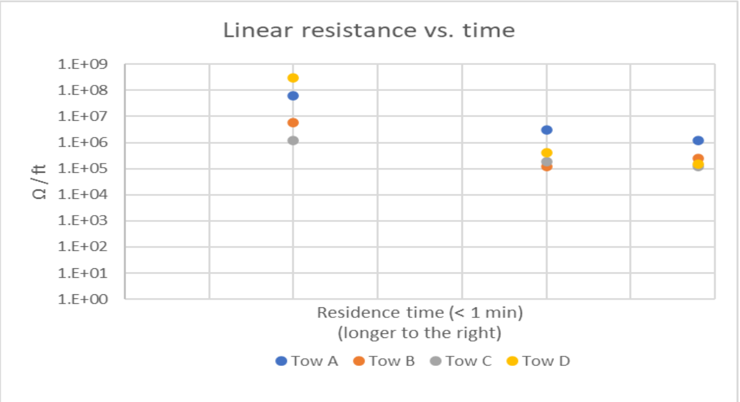
Four 50k tows of oxidized PAN (1.37 g/cc) were processed simultaneously.

Colors indicate same sample from LTC to HTC.



Density vs. residence time at constant power. Run with four tows (A, B, C, D), all residence times shorter than a minute.

Standard deviation is from 1.7% (longest residence time) to 2.4% (shortest residence time).



Linear resistance vs. residence time at constant power. Run with four tows (A, B, C, D), all residence times shorter than a minute.

Data from original proposal (data of reference):

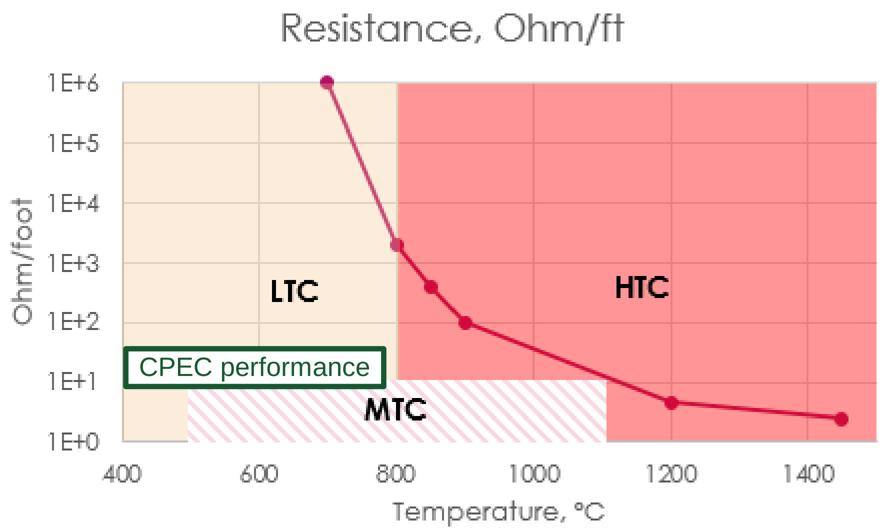
OPF

LTC CONVENTIONAL	
Temp. (°C)	Density (g/cc)
RT	*1.37*
500	1.48
550	1.51
600	1.54
650	1.56
700	1.60
750	>1.60

CPEC performance

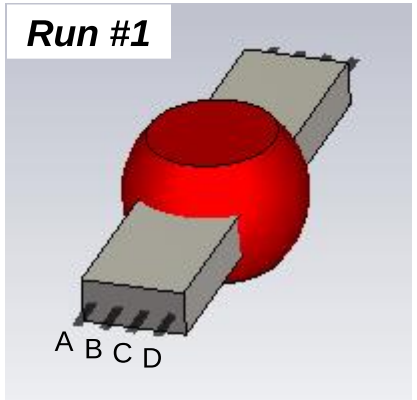
Compare to conventional LTC upper limit, with less than 1 minute, CPEC fiber shows:

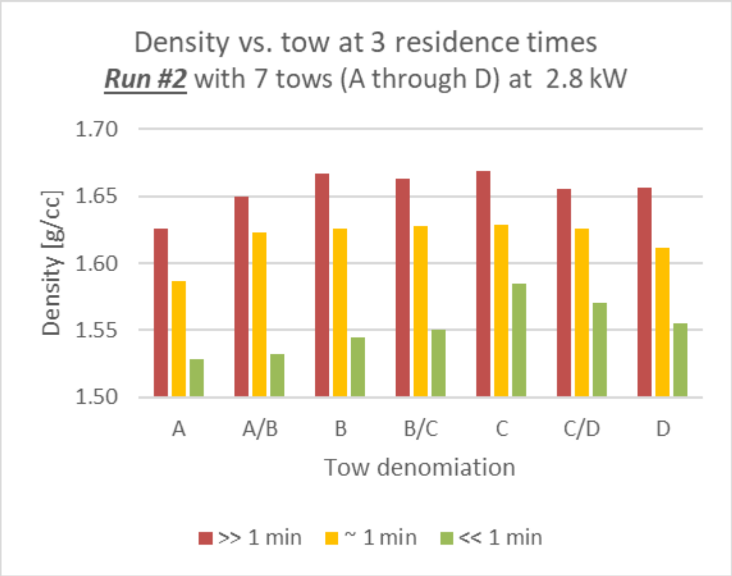
- Higher density
- Slightly lower resistance per unit length

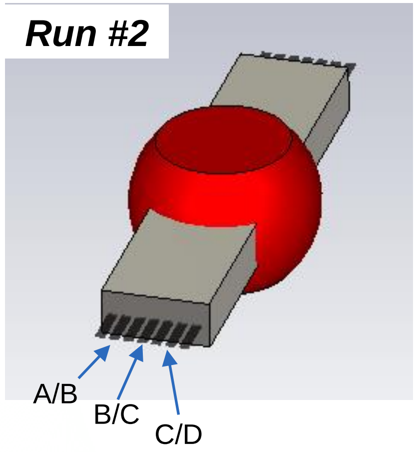


Progress – Operation of "CPEC-4 Configuration #2"

- <u>Performance comparison 4 tows vs. 7 tows (examples)</u>







Density profile of the tows at different residence time. Power is set constant at 2.8 kW; the stretch is also a fixed value.
- On the left: 4 tows (A, B, C, D) are introduced in the cavity; the three residence times are below 1min. A gap exists between the tows.
- On the right: 7 tows are processed. The positions of tows A, B, C, are D are unchanged, but the gaps are filled with three additional tows (A/B, B/C, and C/D).
Times slightly shorter than one minute (~1, in yellow) and substantially shorter than one minute (<< 1min, in dark green) are identical for both runs.

<u>Table:</u> Average values of achieved densities for ***Run #1*** and ***Run #2***
SD: standard deviation

Run #1			***Run #2***		
Residence time	**Av. Density [g/cc]**	**SD [g/cc]**	**Residence time**	**Av. Density [g/cc]**	**SD [g/cc]**
>> 1 min	N/A	N/A	>> 1 min	1.655	0.014
~ 1 min	1.637	0.017	~ 1 min	1.618	0.015
< 1 min	1.624	0.022	< 1 min	N/A	N/A
<< 1 min	1.577	0.024	<< 1 min	1.552	0.020

Progress — Energy consumption

- Literature/publications references:

Energy consumption of conventional process (ORNL, 2012)	
Theoretical furnace characteristics	
Name plate capacity (mT/year)	1,500
Numer of tows (50k filaments)	120
Length (m)	13.5
Process parameters	
Temperature (°C)	700
Residence time (s)	90
Line speed (m/min)	8.96
Estimated unit consumption (industrial conventional process)	
1.74 kWh/lb	

Energy consumption evaluation for a 13.5 m long industrial conventional LTC furnace. [Source: S. Das, ORNL, 2012]

	Goss (1986)	Cohn (2001)	Kline (2004)	Harper (2011)	Trütz-schler (2012)	Das (2012)	This paper (2013)
Precursor	34%	47%	51%	31%	51%	54%	54%
Pretreatment	3%					6%	1%
Stabilization	20%	16%	16%	69%	49%	13%	12%
Carbonization	23%	26%	23%			8%	21%
Surface treatm.	4%	2%	4%			3%	4%
Sizing	7%	2%				4%	4%
Winding	5%	3%	6%			9%	4%
Other	4%	4%	0%			3%	0%

With this calculated consumption of electricity, plus initial capital investment, maintenance and other additional costs, S.Das figured that the cost of conventional LTC and HTC represents 8% of the overall cost of CF in industry. A benchmark shows this cost share of 8% is significantly lower than those in other studies.
[Source: Zhang. Carbon Fiber Production Costing – A Modular Approach. Textile Research Journal. 2014]

- CPEC performance:

CEPC-4 Config #2 Control volume	Energy consumption (kW)	Comments
Applicator — EM energy only	2.8	Most of the energy delivered to the applicator from the generator.
Generator — electrical consumption	6.8	Includes the RF energy delivered to the applicator. The efficiency of the generator is 41% *
Cooling	4*	Cooling of the generator Cool of other components (insignificant)
Conventional heaters	1.2	Are used to prevent tar condensation inside the dampers (adjacent to the process chamber)

* *Better hardware design is needed*

	CPEC-4 Configuration #2 efficiency (kWh/lb) per given control-volums							
Residence time	Applicator EM energy only (2.8 kW)		Generator Elec. consumption (6.8 kW)		Generator + cooling Elec. consumption (10.8 kW)		All system Elec. consumption (12 kW)	
	Run #1 (4 Tows)	**Run #2 (7 Tows)**	**Run #1 (4 Tows)**	**Run #2 (7 Tows)**	**Run #1 (4 Tows)**	**Run #2 (7 Tows)**	**Run #1 (4 Tows)**	**Run #2 (7 Tows)**
T >> 1 min	5.4	3.1	13.1	7.5	20.7	11.8	23.0	13.2
T ~ 1 min	3.2	1.8	7.8	4.5	12.4	7.1	13.8	7.9
T < 1 min	2.7	1.5	6.5	3.7	10.4	5.9	11.5	6.6
T << 1 min	1.8	1.0	4.4	2.5	6.9	3.9	7.7	4.4

Note: CPEC produces fibers already inside of HTC (750°C – 800°C). This additional benefit is not included in this table.

Progress

4 LTC tows (50k ea.) coming out of the applicator CPEC Configuration #2

Response to Previous Year Reviewer's Comments

- Previous year scoring (AMR 2019):
  - 100% of reviewers indicated that the project was relevant to current DOE objectives
  - 100% of reviewers indicated that the resources were sufficient

- Question 1:

Approach to performing the work—the degree to which technical barriers are addressed, the project is well-designed, and well planned.

  - Main point from the four reviewers:
    - R #1: "*… creative approach.*" Thank you.
    - R #2: "*…created a logical approach and a novel method for addressing the energy intensive and long dwell times for LTC… has to be fully proven.*" Despite many challenges, the project proved feasibility.
    - R #3: "*… it appears more challenges were encountered in the CPEC-4 in conjunction with the additional configurations.*" The project encountered many challenges. The exploration of several configurations contributed to the gain of knowledge and the selection of the parameter choices.
    - R #4: "*reliance on a single piece of equipment points to potential fundamental barriers in deploying the technology and scaling it up in the future.*" The main equipment issue of non-conformity to specification was solved, and the applicator was redesigned for a better compatibility. At the end of the project, the unit is 100% operational.

Response to Previous Year Reviewer's Comments

- Question 2:

Technical Accomplishments and Progress toward overall project goals—the degree to which progress has been made and plan is on schedule.

- R #1: "*…ultimately able to show evidence of carbonization… hardware issues are sorted out.*"
- R #2: "*…evidence of carbonization… bringing this on-line will provide more indication of the process' successes, which are not entirely clear, presently.*"
- R #3: "*… demonstrated the feasibility of carbonizing polyacrylonitrile(PAN) fibers using the electromagnetic method… further optimization and scale up proceed.*"
- R #4: "*… mystery around whether model assumptions, supplier failure to meet performance specifications, or anomalies in the precursor inputs are at fault. significant technology gaps remain, which should not be too surprising given the technical readiness level of this important work. The team appears to have a path forward, it has already recovered from the CPEC-4 failure, and that should be recognized.*" The root-cause of the differences between modeling and experimental work could be diverse and difficult to identify, despite the fact that some limitations of both materials in use and modeling are well known. In the present case, in-situ measurement is challenging (high power, high frequency, elevated temperature, etc.)

Our comment to all reviewers:

- Every reviewer concurred that carbonization happened and, despite all the technical challenges, progress was made and a solution is about to be achieved.
- In the last year, the project evaluation was rated at 2.75 on "Technical Accomplishment". It is clearly understandable because measurable results surpassing the programmatic milestones were not available at the time of the preparation of the presentation. They became available after the test phase in late May 2020 and were verbally reported only.

Response to Previous Year Reviewer's Comments

- Question 3:

Collaboration and Coordination Across Project Team.

- R #1: "*… collaboration is appropriate and very well structured.*"
- R #2: "*… very good collaboration and coordination across the project team.*"
- R #3: "*… seems appropriate.*"
- R #4: "*This reviewer scored down the collaboration… When a 2-month period of negotiation is required after a significant equipment failure, this indicates that a program fault may exist. In this case, it clearly has stalled progress.*" The 2 months period of negotiation refers to the time needed by DoE and ORNL to reach agreement about the last extension for this project. The collaboration development/work between ORNL and 4XTechnologies had no influence on this DoE-ORNL procedure.

Answer to all reviewers:

- The collaboration between ORNL and 4XTechnologies is ideal for this type of project: ORNL brings an extensive background and knowledge in material science/CF and their evaluations. 4XT brings engineering background in plasma physics, electromagnetics (including modeling), and hardware construction.

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Response to Previous Year Reviewer's Comments

- Question 4:

Proposed Future Research—the degree to which the project has effectively planned its future work in a logical manner by incorporating appropriate decision points, considering barriers to the realization of the proposed technology and, when sensible, mitigating risk by providing alternate development pathways.

- R #2: "*The reviewer wondered if it is possible and what might be done—beyond simply measuring the resulting fiber—to validate the coulombic efficiency (CE) model output and further inform scaled-up equipment designs. Otherwise, the stated work proposed for FY 2020, including the economic analysis, is important for validating the value of this work.*" As mentioned previously, in-situ measurements are challenging. Hardware modification guided by a large number of computer iterations provided relevant results, such as the production of CF with good mechanical and physical characteristics. This is a clear indication that the scientific and technical approach was an acceptable and reasonable one.
- R #3: "… overall, the approach for the next steps seems reasonable."
- R #4: "… the volume of material promised and how cost is expected to scale with volume is unclear to this reviewer." Design plate capacity of the actual unit: 1 metric ton/year. Cost as a function of volume was unknown at the time of this review. Larger scale is outside of the scope of this project.

Answer:

- ➢ Despite shortcomings with the modeling and hurdles on the physical implementation, this project progressed successfully.

Response to Previous Year Reviewer's Comments

- Question 5:

Relevance—Does this project support the overall DOE objectives?

- R #1: This will drive cost down and expand applications for carbon fiber in transportation resulting in energy savings that align with strategic DOE goals."
- R #2: "The electromagnetic method holds the promise to decrease conversion cost, which this reviewer indicated is the way to reduce the cost of PAN-based carbon fibers for vehicle applications."
- R #3: "The objective of low-cost carbon fiber is in line with DOE objectives."
- R #4: Reducing energy of manufacture is a key DOE goal."

Answer:

➢ *We thank the reviewers for the positive perception of this project.*

- Question 6:

Resources—How sufficient are the resources for the project to achieve the stated milestones in a timely fashion?

- R #1: "The high-risk, high-reward research and development (R&D) appears to be adequately resourced with meaningful results forthcoming.".
- R #2: "The team has sufficient resources"
- R #3: "Some of the updates proposed will further align with resource needs."
- R #4: The extra year given to the team to sort out issues is appropriate.

Answer:

➢ *We agree with the evaluation of all reviewers.*

Collaboration and coordination

ORNL performed this project in collaboration with:

4XTechnologies — Joint development. Equipment construction and experimental work performed at this site.

4XTechnologies is a dynamic startup located in Knoxville, TN, with a core focus on plasma science and engineering and experience in fiber treatment/conversion and environmental applications.

Remaining Challenges and Barriers

- For a scale up of this technology, some additional research/effort will be needed to increase the efficiency of some components of the CPEC sub-systems:
  - Low efficiency equipment consumption (e.g.: generator)
  - Better thermal insulation of the applicator
  - Better selection of dielectric materials
  - Further development of CEM model that encompasses thermal property changes and properties at higher temperature. *Without a CEM model, this work could not have been successful within this project timeframe.*

CEM modeling: computational electromagnetic modeling

Proposed Research

- FY21: High temperature carbonization using EM (HTC)
  - Based on the results of this work, it was proposed* to the DoE to further implement the same technological concept to the High Temperature Carbonization (HTC) conversion stage. With this sequential work, a comprehensive solution for a full carbonization conversion process based on the knowledge achieved with the CPEC technology will be possible.

** Any proposed future work is subject to change based on funding levels*

Summary

- CPEC was a technological challenge, but very successful project:
  - CF met and surpassed the programmatic milestone criteria
  - Energy evaluation was determined
  - Demonstrated a device for 1 ton / year capacity (design)
    - At the end of the project, a capacity of 1.75 ton/year was achieved
  - CPEC technology fully demonstrated
    - Carbonization at LTC level and further
- Project was completed on Sept. 30, 2020 (end of FY2020)
  - 3 last milestones completed on time
  - Project was on budget
- Final project report submitted on Nov. 13, 2020


Mat122
Questions?
Thank you for your attention

Technical Backup

Technical Accomplishments (FY2020)

Continuous Processing of 4 tows with “CPEC-4 Configuration #2” Furnace

Example of mechanical properties of selected samples processed LTC via CPEC and subsequently conventionally HTC*

Process of June 9, 2020						
Specimen ID	*Status*	*Density (g/cc)*	*Diameter (µm)*	*Peak Stress (ksi)*	*Modulus (Mpsi)*	*Strain (%)*
Tow A	LTC only	1.6193 (.0005)	9.03 (0.6)	146.1 (38.9)	5.22 (0.6)	3.10 (0.9)
	HTC condition 1	**1.8138 (.0056)**	**6.81 (0.4)**	**520.4 (106.7)**	**30.6 (0.8)**	**1.63 (0.3)**
	HTC condition 2	**1.8100 (.0016)**	**7.05 (0.4)**	**609.0 (99.4)**	**30.9 (0.9)**	**1.87 (0.3)**
Tow C	LTC only	1.6143 (.0008)	8.74 (0.4)	160.0 (17.3)	5.09 (0.3)	3.54 (0.6)
	HTC condition 2	N/A	**6.88 (0.4)**	**524.9 (66.3)**	**30.1 (1.2)**	**1.67 (0.2)**
Tow D	LTC only	1.5685 (.0005)	9.17 (0.3)	121.0 (17.6)	3.77 (0.2)	4.37 (0.9)
	HTC condition 2	N/A	**6.97 (0.5)**	**535.7 (90.7)**	**30.1 (1.0)**	**1.70 (0.2)**

In blue: mechanical properties of samples that were processed with CPEC-4 (LTC) only.

In black: the same samples were further processed conventionally HTC with one or two conditions

* HTC: conventional High Temperature Carbonization

Technical Accomplishments (FY2018)

Already presented

Continuous Processing of Fiber with CPEC-3 Furnace

Mechanical properties of fully carbonized fiber (as of 11/2017)

Oxidation (conventional), LTC (CPEC-3), HTC (Conventional)*

Test#	Density (g/cc)	Diameter (Avg) µm	Std. Deviation	Tensile Strength (Avg) ksi	Std. Deviation	Modulus (Avg) Msi	Std. Deviation	Strain (Avg) %	Std. Deviation	Residence Time
1	1.8032	8.05	0.35	348.70	77.50	23.42	1.84	1.49	0.28	Long
2	N/A	8.20	0.41	303.00	87.50	22.73	2.76	1.40	0.32	Short
2	1.7924	8.44	0.74	356.60	135.30	24.88	3.83	1.42	0.47	Long
2	N/A	8.00	0.80	254.20	88.90	21.42	2.59	1.22	0.43	Long
3	N/A	8.40	0.53	333.00	149.80	25.44	3.45	1.29	0.51	Short
3	N/A	8.22	0.63	292.00	91.70	22.79	3.31	1.27	0.27	Short
3	N/A	8.42	0.46	331.30	125.00	23.44	1.84	1.48	0.55	Long
4	N/A	8.09	0.62	354.60	97.60	23.64	2.42	1.48	0.32	Short
4	N/A	8.06	0.72	263.60	132.80	22.31	3.61	1.13	0.44	Short
4	1.8138	8.91	0.63	340.20	101.70	25.14	1.73	1.39	0.43	Long
4	1.8135	8.73	0.56	285.50	98.50	23.07	2.03	1.23	0.37	Long

Table 1: Mechanical properties of fully carbonized samples at HTC. All residence times in CPEC-3 are shorter than 90 seconds. The values highlighted in green surpassed the dual programmatic requirements of 250ksi tensile and 25Msi modulus simultaneously.*

* HTC: High Temperature Carbonization